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# Growth of Solid Solution Single Crystals

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## TECHNICAL PAPER

# GROWTH OF SOLID SOLUTION SINGLE CRYSTALS

## INTRODUCTION

The technological utility [1] and the scientific interest [2-7] in  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  have been well documented. Likewise, the difficulty in growing bulk, compositionally homogeneous material by directional solidification is widely recognized [2,5-9]. This paper discusses the reasons that Bridgman and related directional solidification methods normally fail in the presence of Earth's gravity and shows that in such a gravitational environment it is nearly impossible to grow crystals that are both radially and axially homogeneous for significant crystal lengths. Because the HgTe-rich component rejected during solidification is more dense, the vertical Bridgman-Stockbarger growth process would appear to be both gravitationally and thermally stable against convection, but this is not generally true. Due to the peculiar relationships between the thermal conductivities of the melt, solid, and ampule, it is practically impossible to completely avoid radial temperature gradients in the growth region [2]. Thus, in spite of the stabilizing influence of the solutal density gradient, significant thermosolutally driven fluid flow occurs in a narrow region near the interface [10]. It is expected that under reduced gravity conditions,  $g \lesssim 10^{-5} g_0$ , such flows can be significantly suppressed to yield a corresponding reduction in the associated radial composition gradients in the solidified crystals.

In general, the presence of radial temperature gradients near the growth region will cause a curvature in the solid-liquid interface which need be neither an isothermal nor an isoconcentrational surface. Furthermore, the growth of high quality crystals usually requires a slightly convex growth interface as viewed from the melt [11]. Under the influence of stable growth conditions, such interface geometries readily lead to lateral alloy segregation because of the tendency of the more dense HgTe-rich liquid to settle at the portions of the surface having the lowest gravitational potential. Because the alloy solidus temperature decreases with increased HgTe content, the interface temperature will be lowered in this region, causing the interface curvature to increase. Although lateral diffusion will tend to drive the interfacial melt compositions to some equilibrium values, most ground-based melt-growth experiments show large radial compositional variations that are probably a direct consequence of such an interfacial fluid flow phenomenon [3,5-9,12]. Although the growth at very slow rates, under the influence of reduced stabilizing composition gradients and thus non-steady flow conditions, yielded radially more homogeneous ingots [8], no ingots could be obtained by the Bridgman-Stockbarger method that were simultaneously axially homogeneous for any length. This paper discusses a method developed and used to obtain various desired interface shapes in  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  and other II-VI solid solution alloys. It is expected that the method, when combined with reduced stratification effects, will yield crystals with improved compositional uniformities and reduced line defect densities. Finally, the properties of  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  and other similar alloy semiconductors impose some specific requirements on space flight hardware and experiment design. These will also be discussed.

## CONVENTIONAL APPROACH TO VERTICAL BRIDGMAN GROWTH

The conventional Bridgman-Stockbarger method usually uses a wide adiabatic zone between the hot and cold zones of the growth apparatus [11]. This method yields the desired flat isothermal surfaces for situations where the thermal properties of the solid and melt, particularly the thermal conductivity, are the same or where the thermal effects of the ampule can be neglected. Unfortunately, neither of these conditions apply for  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ . The thermal diffusivity varies substantially with both composition and temperature [13] and the thermal conductivity of the requisite fused silica ampule is comparable to that of the material [14]. An example of the effect of different thermal conductivities is shown in Figure 1. Because of the generally higher thermal conductivity in the melt than in the solid, the use of a wide adiabatic zone will produce isothermal surfaces near the interface that are bowed downward into the solid, as shown. Although the interface under this condition will be neither an isothermal nor an isocompositional surface, it will be bowed in the same direction as the isotherms near it. This will lead to the collection of HgTe-rich liquid at the low region of the interface and thus the HgTe-rich centers in radial slices that are generally, although not universally [2,15], reported for Bridgman grown  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ . This effect has been discussed elsewhere [2].

## AN IMPROVED BRIDGMAN GROWTH METHOD

During this investigation, we have developed a method for the vertical growth of  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  and similar alloys that minimizes the problems with the conventional method outlined above [2,3]. This method depends on the careful control of the radiation heat transfer near the growth interface. This is achieved by using a thin ( $\sim 4$  mm) thermal barrier between the hot and cold zones of the growth apparatus and by the judicious choice of the growth temperatures [2]. Each zone is provided with an isothermal furnace liner (heat pipe) to assure isothermality of the zone. A detailed description of the heat transfer during growth has been given in Reference 2. There it is shown that the interface can evolve during growth from concave (viewed from the melt) to convex and back to concave by selection of a proper set of growth parameters. This type of evolution is shown in Figure 2.

It is believed that this method, when used in a microgravity environment, will yield single crystalline material which is simultaneously homogeneous in both the axial and radial directions. The relative simplicity of the method makes it the choice for evaluating the potential benefits of growing  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  and similar materials in microgravity.

## RESULTS AND DISCUSSION

Over the past several years, a detailed evaluation has been performed of the effects of growth parameters on the axial and radial compositional uniformity in directionally solidified  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  and other similar pseudobinary alloys. To obtain a measure of the relative importance of the various heat and mass transfer processes involved, detailed radial and axial composition profiles have been obtained for many ingots. The axial compositional profiles for a series of  $x = 0.2$  and  $0.4$  ingots have been deduced from precision density measurements [9,16] and have been described previously. One example is shown in

Figure 3. Additional profiles, including some for  $x = 0.6$  ingots, have been measured more recently. All profiles that did not suggest interface breakdown could be fit well by a set of one-dimensional diffusion equations [3,8,9,17-19]. Furthermore, the best values ( $4.5 \times 10^{-5}$  to  $6.0 \times 10^{-4}$  cm<sup>2</sup>/s) for the effective diffusion coefficient,  $D$ , did not show any significant growth rate or other growth parameter dependence. Most of the samples grown were 5 mm in diameter and it is suspected that the effective diffusion coefficient would vary with diameter. Nonetheless, these results suggest that the expected convective flows resulting from curvature in the growth interface and horizontal temperature gradients did not penetrate the entire melt column.

In some ingots, the axial composition profile showed evidence of interfacial breakdown. This was manifested by a sudden increase in Cd content near the last-to-freeze end of the ingot. Because of the strong correlation between this effect and the temperature gradient to growth rate ratio, doubtless the observed effect is due to interfacial breakdown. Either the interface becomes dendritic and convection currents cause the CdTe-rich dendrites to break off and rise to the top of the melt or small, CdTe-rich particles are homogeneously nucleated slightly above the interface and then rise. The latter is possible because the variation in thermophysical properties with composition and temperature permit a condition where the melt is constitutionally supercooled slightly above the interface but not at the interface. For example, the thermal conductivity increases sharply just above the interface [2]; this reduces the temperature gradient away from the interface more rapidly than if the thermal conductivity in the melt were constant.

Extensive infrared transmission edge and x-ray energy dispersion measurements were used to assess the magnitude of radial segregation [3,8,9,12]. The segregation showed a definite growth rate,  $R$ , dependence, with the most pronounced effect occurring for the slowest growth rates. This effect is illustrated by the results for two  $x = 0.2$  ingots L6 and L7. The radial compositional data for several slices from each ingot are shown in Figure 4. Both ingots were grown under identical conditions except for the growth rate. L6 was grown at a rate of 2.68 cm/day and had total radial composition variations of about 0.05 in  $x$  over most of its length. L7 was grown at a rate of 0.59 cm/day and had total variations of less than 0.0025 in  $x$  between 3 and 10 cm from the first-to-freeze end [8]. Similar growth rate dependences have been observed for higher alloy compositions, also.

Several years ago, it was proposed that the vertical extent of the convective region above the crystal growth interface must be small compared to the effective diffusion length,  $\sim 2D/R$  [12], because of the good fit of the axial compositional variations to a one-dimensional diffusion model as discussed above. A more recent investigation of the similar Ge-Si alloy system by Rouzaud, et al. yielded similar conclusions [20]. Rouzaud, et al. have also shown that these observations are in accord with the results of Hart's [10] stability analysis of saline solutions having stabilizing compositional gradients and horizontal thermal gradients. For our growth conditions, the thermal and solutal Rayleigh numbers for the melt near the interface are estimated to be about  $10^4$  and  $10^6$ , respectively. A stability analysis of Hart's type thus implies flow characteristics that may straddle the critical stability curve depending on the choice of the exact growth conditions. In agreement with the conclusions suggested by the experimental results [12], such an analysis also suggests that the extent of the flow region should be about a factor of 10 smaller than the estimated size of the effective diffusion lengths involved. This type of analysis also suggests that for  $g$ -values less than  $10^{-5} g_0$ , the residual flow velocities can be made to be more than a factor of 10 smaller than the proposed interface translation rates ( $\sim 0.4$   $\mu$ m/s).

Coriell and Sekerka [21] have shown that under steady conditions, the radial variation in composition is given by

$$\delta C = C_o[(k-1)/k] (R/D) \delta z \quad (1)$$

and that  $\delta z$ , the vertical bowing of the interface, is determined by the thermal conditions alone.  $C_o$  is the overall melt composition and  $k$  is the interface segregation coefficient. Assuming the same  $\delta z$ , equation (1) yields a ratio in  $\delta C$  for L6 to L7 that is about a factor of 5 smaller than the measured value. It was concluded thus that the difference in radial segregation between L6 and L7 is probably due to a transition to a time-dependent flow region as  $R$  is reduced and not to the steady state condition considered above. It is worth noting that the temperature distribution at the interface during  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  growth is growth rate dependent because of the composition and temperature dependence of the thermophysical properties so that  $\delta z$  is expected to depend on growth rate. Recent numerical simulation of the complete heat flow problem [22] suggests, however, that this effect is probably less significant than previously assumed [2].

### ADVANTAGES OF A LOW-GRAVITY ENVIRONMENT

Frequently, the desirable surface geometry for crystal growth is planar or nearly so. Usually, however, the optimum interface shapes tend to be those that bow slightly into the melt [23] because these shapes are expected to produce ingots with better crystal perfection. While such shapes are difficult to achieve for  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ , it can be done with judiciously chosen thermal boundary conditions [3,15]. Nonetheless, such an interface is highly susceptible to interface runaway and usually leads to CdTe enrichment in the center for the same reasons that an interface that is bowed into the solid produces slices with HgTe-rich centers [3,5-9,12].

In microgravity it is expected that the highly desired slightly convex growth surfaces will be easier to maintain because of the reduced tendency for stratification of the denser (HgTe-rich) fluid component. At the same time, the near-elimination of radial temperature gradient-driven convection is expected to provide for a better control of the lateral compositional distribution in the melts. We thus expect that by growing under the influence of low-gravity conditions ( $g \lesssim 10^{-5} g_o$ ), crystals with significantly improved crystallinity and compositional homogeneity can be prepared as compared to the best crystals that can be produced on Earth. It is also reasonable to expect that careful characterization of both the space- and ground-grown materials will lead to better insights into the peculiarities of the various growth mechanisms that will permit improvements in Earth-based processing of  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  and other compound semiconductor alloy systems.

It has been suggested [24] that CdTe,  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ , etc. probably possess extremely small yield strengths near their growth temperatures. If this is the case, the high dislocation density ( $\sim 10^5 \text{ cm}^{-2}$ ) usually seen in these crystals could be due to stresses induced by the samples own weight, that is, self-induced stresses. Although it is not a major goal of the present experimentation, an effort will be made to assess the validity of this hypothesis.



## FLIGHT EXPERIMENT IMPLEMENTATION

Throughout this paper, the importance of careful control of the thermal environment near the growth interface has been emphasized. Thus, to assure the incorporation of these capabilities into the flight hardware, a prototype crystal growth system has been developed in our laboratory by B. R. Aldrich and a flight-qualified version is now in the process of construction. The prototype, shown in Figure 5, has been used to grow crystals of several semiconducting materials including  $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$  and doped Ge. Precise thermal field and interface shape control has been demonstrated. The growth system includes five active thermal control points and two passive control features. This degree of control is necessary to compensate for the lack of heat pipes and yet provide the necessary temperature profile to obtain the desired interface geometries. Heat pipes are used in ground-based studies and are planned for a future flight furnace.

The restrictions imposed by constitutional supercooling and the wide separation between the liquidus and solidus of the HgTe-CdTe phase diagram limit the maximum allowable growth rate to 0.6 to 1.0  $\mu\text{m/s}$  for reasonable values ( $\sim 100$  to  $150^\circ\text{C/cm}$ ) of the applied axial temperature gradient. 0.4  $\mu\text{m/s}$  has been selected for the initial growth rate to allow for a likely decrease in the effective "diffusion rate" because of the reduced flow contribution. Several growth rate changes are being planned for the first flight experiment. A careful analysis of the resulting transient in compositional distributions will be used to establish interface geometries for given growth conditions and to ascertain the effects of growth rate on the radial and axial compositional variations under nearly diffusion limited conditions.

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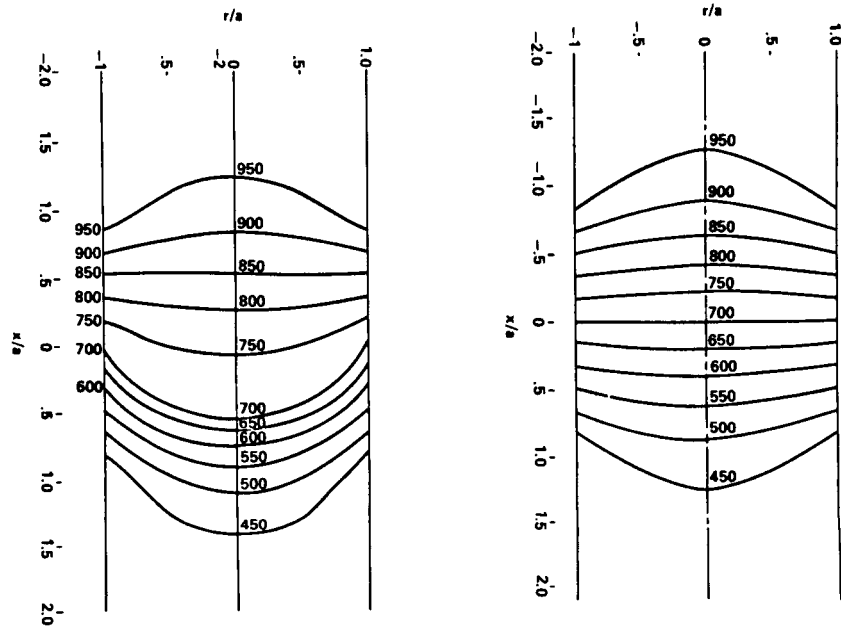


Figure 1. Effect of higher melt thermal conductivity on isotherms. Upper and lower zone temperatures of 1000 and 400, respectively, are used with a  $2x/a$  thick adiabatic zone centered at 0. Notice how the melting point isotherm of 700 changes from the right-hand, equal thermal conductivity case to the left-hand case where the thermal conductivity in the melt is 7 times that in the solid.

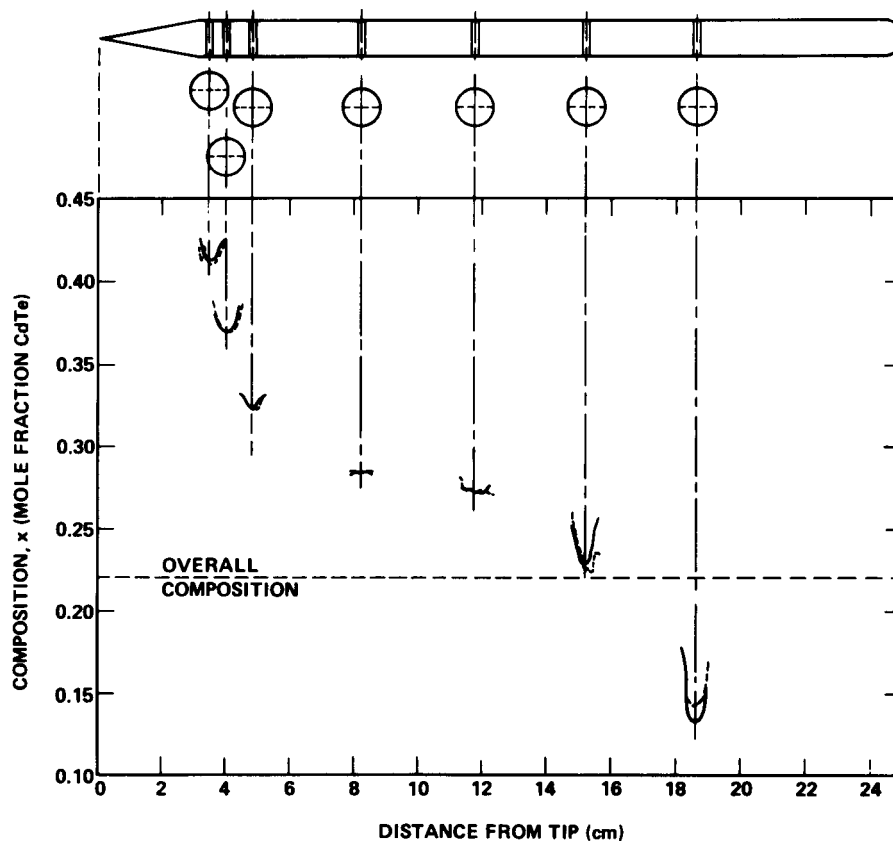


Figure 2. Radial compositional variations from seven slices from a 1-cm-diameter ingot grown according to the improved Bridgman method suggested in this paper. The two curves for each slice show the composition on the same scale as the horizontal axis. These curves show the evolution of the interface during growth from concave to flat or slightly convex and back to concave.

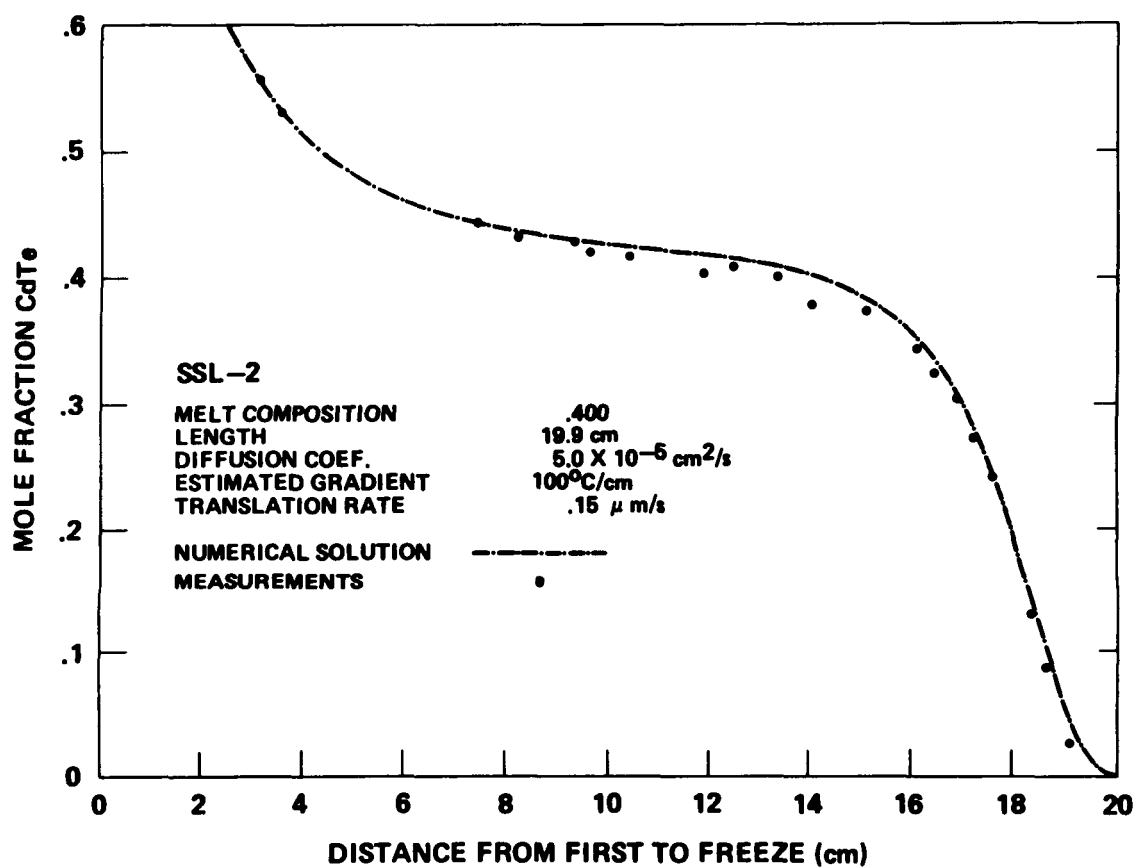


Figure 3. The fit of a one-dimensional diffusion model to axial compositional data for a slowly-grown ingot.

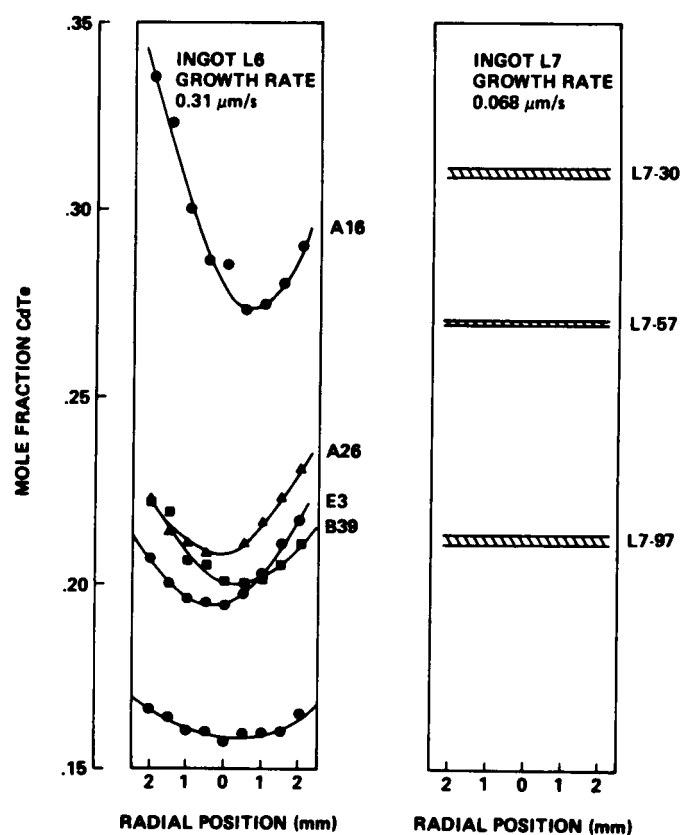


Figure 4. Comparison of two  $x = 0.202$  ingots grown under identical conditions except that the growth rates were different as indicated in the figure. For ingot L6 the curves connect measurements for each of five slices. For ingot L7 the bands indicate the spread of compositions for each of three slices.

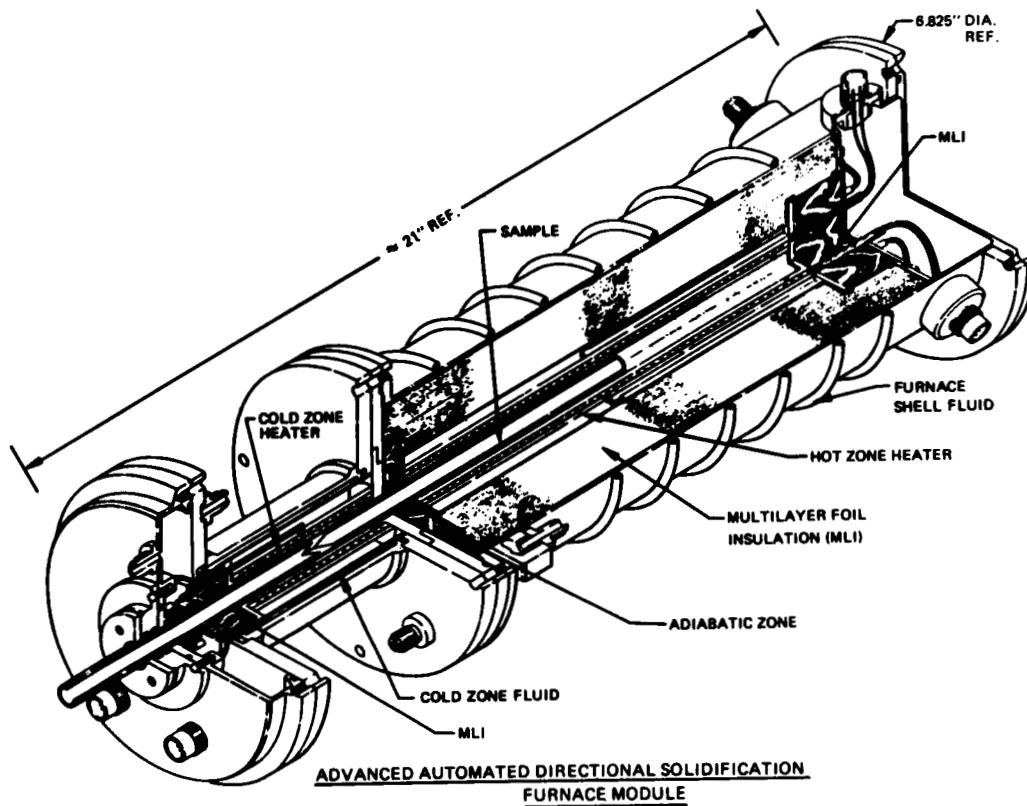


Figure 5. Cutaway drawing of the AADSF laboratory version.



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16. ABSTRACT  Based on the thermophysical properties of $Hg_{1-x}Cd_xTe$ alloys, the reasons are discussed for the failure of conventional Bridgman-Stockbarger growth methods to produce high quality homogeneous crystals in the presence of Earth's gravity. The deleterious effects are considered which arise from the dependence of the thermophysical properties on temperature and composition and from the large amount of heat carried by the fused silica ampules. An improved growth method, developed to optimize heat flow conditions, is described and experimental results are presented. The problems associated with growth in a gravitational environment are discussed. The anticipated advantages of growth in micro-gravity are given and the implications of the requirements for spaceflight experiments are summarized.					
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